PREPARATION OF ANTHRARUFINE

BY

D. H. PODOLSKY

W. E. MEAD

ARMOUR INSTITUTE OF TECHNOLOGY

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THE PREPARATION OF ANTHRARUFINE

A THESIS

PRESENTED BY

DAVID HENRY PODOLSKY AND WALTER E. MEAD

TO THE

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APPROVED:

A. M. McCormack
Professor of Chemical Engineering

Dean of Engineering Studies

Dean of Cultural Studies

ILLINOIS INSTITUTE OF TECHNOLOGY
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OUTLINE.

	PAGE
PREFACE	1
THEORY	4
SULPHONATION	4
NITRATION	10
PYRIDINE	14
ANALYSIS OF FUMING SULPHURIC ACID	16
PATENTS	21
PROPOSED METHODS	38
EXPERIMENTAL WORK	44
DISCUSSION OF EXPERIMENTAL WORK	56
BIBLIOGRAPHY	61

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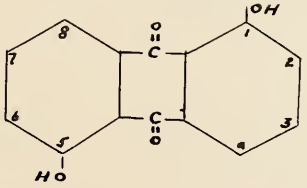
PREFACE.

The subject of the thesis is the preparation of Anthrarufine or scientifically known as 1:5 dihydroxy-anthraquinone.

The structural formula is:



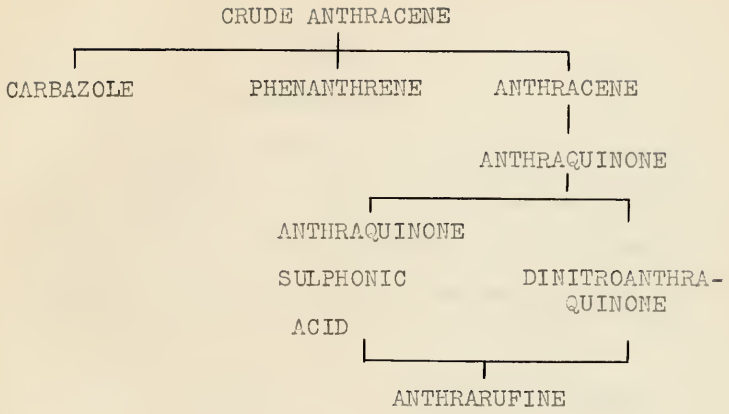
i.e. $C_{14}H_6O_2(OH)_2$

The authors at first set out to prepare a fast blue dye by successive sulphonation, nitration, and reduction of anthrarufine. The market was searched but no anthrarufine could be found. Acting on the advice of Professor McCormack we took up the problem of making the intermediate - Anthrarufine.

The authors wish to express their gratitude and indebtedness to Professor McCormack for his co-operation in the work of the thesis.

The authors also wish to express their

gratitude to Professor B. B. Freud for his aid in the investigation.

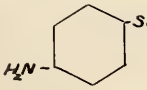

CRUDE ANTHRACENE
CARBAZOLE
PHENANTHRENE
ANTHRACENE
ANTHRAQUINONE
ANTHRAQUINONE SULPHONIC ACID
DINITROANTHRAQUINONE
ANTHRARUFINE

THEORY.

Sulphonation.

Aromatic compounds possess the characteristic property of forming sulphonic acids on treatment with strong sulphuric acid. Thus benzene passes into benzene-sulphonic acid:

The sulphonic group is strongly negative and upon entering into the aromatic hydrocarbon, converts it into a strong acid. In cases where there is a basic group as in sulphanilic acid,



its acid influences completely neutralizes the basic property of the NH_2 group, and thus sulphanilic acid shows acid properties.

Sulphonation in general depends upon the nature of substances to be sulphonated. In such a manner the strength of the acid and the temperature of sulphonation is determined. In cases

with which the authors are dealing, the sulphuric acid contains as high as 60% free SO_3 while there are cases where sodium bisulphate is sufficient for the sulphonation.

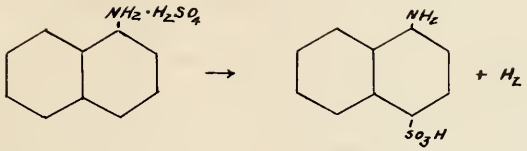
General methods of introducing SO_3H group:

1. Method described by Gotterman consists in preparing a sulphinic acid group (SO_2H) by the action of finely divided copper on a diazo-solution saturated with sulphur dioxide, and then oxidizing the product with alkaline permanganate.

2. The method used particularly in the preparation of naphthalene polysulphonic acids consists in oxidizing the sulphur substitution compounds of the naphthalene sulphonic acids. These are obtained from the corresponding amido compounds by the treatment of diazo salts with potassium xanthate, $K(C_2H_5)CS_2O$, and then hydrolyzing the product with an alkali.

In the cases of the manufacture of naphthionic acid the so-called "leaking process"

is being used. The process consists in roasting the acid sulphate of a base.

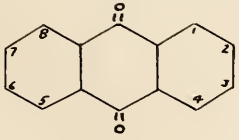


a-naphthylamine acid sulphate naphthionic acid.

3. The direct use of sulphuric acid of various strengths and of various concentrations of free SO_3 depending on individual cases is mostly adopted.

Substitution Products.

Benzene, naphthalene, and anthracene series in its behavior with reagents, resemble each other closely. The opportunity for isomerism is greater in the presence of more than one ring. If we take anthraquinone for example we find that there are two forms of mono-substitution products, alpha and beta.



The carbon atoms numbered 1, 4, 5, and 8 bear the same relation to the molecule. Compounds which contain a group in these positions are known as the alpha-compounds. The carbon atoms numbered 2, 3, 6, and 7 are alike and substitution in one of these positions yield beta-compounds. Ten di-substitution products are possible in the case of compounds which contain two similar substituents; if the substituents are unlike, fourteen di-substitution products are possible.

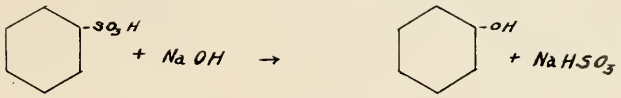
Separation of Sulphonic Acids from excess Sulphuric acid used in the Sulphonation.

The most effective methods of separation are:

1. Precipitation of the sulphuric acid from its solution by means of a saturated solution of potassium or sodium chloride.
2. Treating the mixture of sulphuric acid and the sulphonic acid with calcium, barium, or metal carbonates and then filtering. Sulphonic acids in many instances form soluble salts with metals which pass through in solution while the sulphates remain.
3. There are cases where the sulphonic acid is insoluble in cold sulphuric acid and in such a case it is only necessary to filter the solution through glass-wool or asbestos.

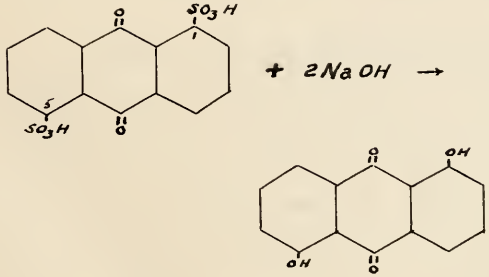
Reactions.

The most important reactions of the sulphonic acid group is the conversion into the hydroxyl group, (OH). This can be attained by fusion with alkali or by heating with alkali under pressure. An example is as follows:



Benzene sulphonic acid Phenol

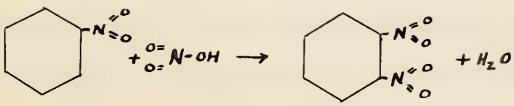
Another example of the conversion of sulphonic group into the hydroxyl is illustrated by the heating of 1:5 disulphonic anthraquinone with sodium hydroxide (NaOH) under pressure.



Nitration.

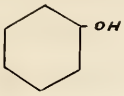
The action of nitric acid is characteristic of aromatic compounds. It may generally be represented by the following equation:

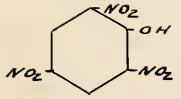
Further action produces bodies of more than one NO_2 group, thus:

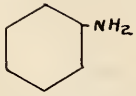


In many cases nitration takes place with great ease, and the action of diluted acid is sufficient, while in other cases the presence of sulphuric acid is necessary before nitration can be effected. In nitrating a compound, a mixture of nitric and sulphuric acids

may be added, or we may first dissolve the substance in sulphuric acid and then add nitric acid or sodium nitrate to it.

The nitro-compounds of the hydrocarbons are indifferent neutral substances like the hydrocarbons. The nitro group upon entering the aromatic body, already containing an acid or a basic group, modifies the reaction of these groups greatly. An example of the above is phenol, 

a sufficiently strong enough acid to form a stable salt with caustic soda, but not sufficiently strong enough an acid to decompose carbonates. But when phenol is converted into trinitrophenol 

it becomes a stronger acid and reacts with the carbonates. It may also be just the reverse of the above case. This is illustrated in the case of 

aniline, which upon nitration into nitroaniline becomes much less basic.

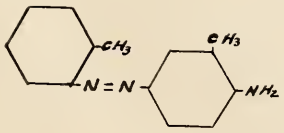
One of the chief reactions of the nitro group, and one which is greatly important in the preparation of dyestuffs and intermediates is its behavior on reduction. The reduction is brought about according to the following equation:

$$RNO_2 + 3H_2 \longrightarrow RNH_2 + 2H_2O$$

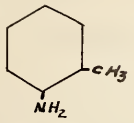
Any acid reducing agent may be employed for that purpose. Iron, owing to its cheapness, is used extensively.

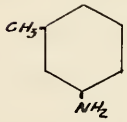
$$RNO_2 - 3Fe - HCl \longrightarrow RNH_2 - FeCl_2 - H_2O$$

Another interesting method of introducing amino groups is used in the reduction of azo compounds. O-toluidine is an example of the above. It is a by-product in the manufacture of magenta. On treatment with nitrous acid in the presence of small quantities of mineral acid, it is converted into amido-azo-toluene.



On reduction it splits up at the N double bond, giving a mixture of O-toluidene and P-toluidene.





The mixture of the two bases is used in the preparation of safranine.

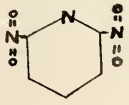
A very interesting method of substitution of the nitro group (NO_2) by hydroxyl is illustrated by the action of pyridine on 1:5 dinitroanthraquinone.

Pyridine - Its Properties and Reactions.

It is one of the basic constituents of "light oil" obtained from coal-tar distillate. Pyridine is a liquid miscible with water, which possesses a characteristic unpleasant odor; it boils at 116° C. and has the specific gravity 0.985 at 15° C.

Pyridine is a tertiary amine; its aqueous solution shows an alkaline reaction and precipitates the hydroxide of metals, some of which are soluble in an excess of the amine.

Pyridine is a very stable compound and may be heated with nitric acid or chromic without undergoing change. Pyridine acts as a strong alkali compound and based on this property that it is used in the replacement of NO_2 in anthraquinone ring by OH. The reactions may be explained as follows:

The pyridine acts on the dinitroanthraquinone as an alkali forming anthrarufine and pyridonium nitrate  which due to

high temperature decomposes into pyridine and nitric acid. The pyridine is then distilled off by steam and the anthrarufine extracted by dilute sodium nitrate.

Analysis of Fuming Sulphuric Acid.

Fuming sulphuric acid is a mixture of sulphur trioxide and sulphuric acid (H_2SO_4).

A sample of the fuming sulphuric acid was transferred to a narrow mouthed stoppered bottle. To weigh out a sample the following method was used: An ordinary test tube was drawn out about 2 inches from the bottom to a fine capillary tube about 2 inches long. The tube was then weighed and the end of it dipped into the acid. The bulb was then heated and on cooling it absorbed some of the fuming sulphuric acid which on being sealed and cooled in a desiccator and then weighed showed a weight of 6.55 gms. net.

The sealed tube was then dropped into a bottle containing 200 cc. of distilled water. The stopper was replaced and by shaking the tube was broken and the white fumes of SO_3 absrobed by distilled water. It was then diluted to 1000 cc.

250 cc. of the solution was then titrated with N/1 sodium hydroxide solution using methyl orange as its indicator.

One cc. of Normal sodium hydroxide solution contains .040 gm. NaOH and it neutralizes 1/2 molecule SO_3 and a whole molecule of SO_2. That is, 1 cc. normal sodium hydroxide will neutralize .040 gm. of SO_3 and .064 gm. of SO_2.

In the titration 36.5 cc. of normal sodium hydroxide was used.

Another 250 cc. of the sulphuric acid (fuming) solution was titrated with N/10 iodine solution using starch as indicator.

One cc. of N/10 iodine solution corresponds to .0032 gm. SO_2, therefore, for each cc. of iodine used .05 cc. must be subtracted from the number of cc. of normal caustic soda used in the first titration in order to obtain the correct amount of SO_3 present.

Determination of SO_2.

2.3 cc. of N/10 iodine solution was used which corresponds to

$$2.3 \times .0032 = .00736 \text{ gm. } SO_2$$

Sample used was $\frac{6.55}{4} = 1.64$ gm.

Hence the sample contains

$$\frac{.00736}{1.64} \times 100 = .444\% \ SO_2$$

Since SO_2 is present we must deduct the equivalent of sodium hydroxide

$$2.3 = .05 = .115 \text{ cc. NaOH.}$$

In this case it is neglected for being a very small quantity.

Determination of SO_3.

Sodium hydroxide used = 36.5 cc.

This is equivalent to

$$36.5 \times .04 = 1.4612 \text{ gm. } SO_3$$

Sample used is 1.64 gm.

Hence the sample contains

$$\frac{1.4612}{1.64} \times 100 = 89.1\% \ SO_3$$

Thus the analysis shows

89.1% SO_3 .444% SO_2 10.46% H_2O.

From the following equations

$H_2O + SO_3 \quad H_2SO_4$

18 80

It is seen that in order to form one molecule of sulphuric it is necessary to use $\frac{80}{18}$ or 4.44 gm. SO_3 to the water molecule which is taken as 1. Hence the water combines with

$10.46 \times 4.44 = 46.44\%\ SO_3$

So that the acid contains

$89.10 - 46.44 = 42.66\%\ SO_3$

The complete analysis of our acid is therefore

H_2SO_4	56.90
SO_3	42.66
SO_2	.44

The acid was made up to its full strength by the use of solid 100% SO_3 which was prepared by the authors.

The concentration was done according to the following formula:

- Let:

X = weight of solution of C% concentration that will be diluted by adding to it Z grams of an A% solution necessary to make a quantity Z + X grams of a solution stronger than the A% solution and of a D% concentration.

$$CX + AZ + D(Z + X)$$

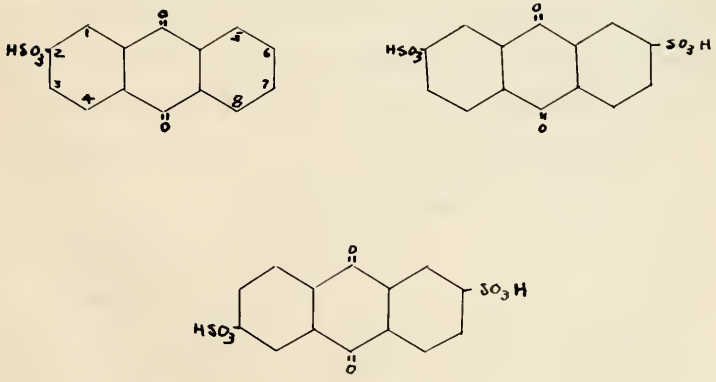
$$X(C - D) = Z(D - A)$$

$$X = \frac{Z(D - A)}{(C - D)}$$

E. P. 10242 - A.D. 1903.

Theory.

If anthraquinone be sulphonated with sulphuric acid, the SO_3H groups appear always in the m-position and never in the o-position relatively to a CO group. When two SO_3H groups are introduced, they are divided between the two cores or nuclei. Consequently only the three possible acids can be produced, namely a mono-sulpho-acids and two di-sulpho-acids, of the following constitution:



We have now been successful by means of the addition of comparatively small quantities of mercury or mercury compounds to deflect or modify the sulphonation process in such a manner as to cause the sulpho group to take up other isomeric positions. At the same time the sulphonation process takes place much more readily in the presence of mercury than without mercury. In the case of anthraquinone for instance, o-anthraquinone sulpho-acids are produced with the greatest ease by means of the addition of exceedingly small quantities of mercury compounds. The reaction takes place smoothly and the o-sulpho acids are produced at once in a condition of the greatest purity with a very abundant yield.

Specifications.

500 parts of Anthraquinone

5 parts of Mercury

1000 parts of fuming Sulphuric Acid containing 40% of free SO_3, are heated slowly to a temperature of 160°, and kept at this temperature for one

hour. The whole of the anthraquinone is then converted into water-soluble sulpho-acids. The fluid mass when cool, is stirred into about 4500 parts of cold water and it then contains a series of o-disulpho-acids together with some o-mono-sulpho-acid, but it consists for the greater part of the anthraquinone 1:5 sulpho-acid. The separation of the sulpho-acids may be effected in various ways.

For instance, the whole mass may be neutralized, after suitable dilution, with lime, freed by filtration from the precipitated gypsum and then either the lime salts are separated out as such, or they are first converted into alkaline salts. At first the salts of the o-mono-sulphoacids and of the 1:8 disulpho-acid are separated out. The middle largest fraction contains mainly the 1:5 disulpho-acid. In the last mother liquors there still remain, besides some 1:5 disulpho-acid, at least two new di-sulpho-acids, of which one was definitely

determined as being 1:7 disulpho-acid leading to m-benzdioxy-anthraquinone.

The m-sulpho-acids which are exclusively formed in the ordinary sulphonation process, could not be found at all or at least only as traces in the mercury-sulphonations.

The products namely chrysazine and anthrarufine obtained by melting the corresponding fractions of the 1:8 and 1:5 di-sulpho-acid salts with lime have been identified as such.

Conclusions.

The claim is:

1. The manufacture of organic sulpho-acids according to which mercury or mercury compounds is or are added to the sulphonating mixture whereby the sulpho group is caused to enter the molecule in positions that have hitherto been impracticable or almost so, by direct sulphonation.

2. The manufacture of organic sulpho-acids by adding mercury or mercury compounds to the

sulphonating mixture substantially as herein-before described with reference to specific examples.

E. P. 13808 - 1903.

Specifications.

A finely powdered mixture of 100 parts of anthraquinone and one part of mercuric oxide is mixed with 200 parts of fuming sulphuric acid (40% SO_3) and the resulting mass is slowly heated. At about 110 - 120° C. a reaction sets in. One must take care of the temperature that it does not exceed 160 - 170°. It is kept at this temperature until a test portion is soluble in water and until all sulphuric anhydride may be totally or nearly disappeared. During the heating the $alpha_1$ - $alpha_3$ anthraquinone disulphonic acid separates out in the shape of large quadratic plates, while the $alpha_1$ - $alpha_4$ disulphonic acid remains dissolved. It is allowed to cool down about 30o C.; the melt is mixed with 75 parts of sulphuric acid 66° Be and the $alpha_1$ - $alpha_3$ disulphonic acid is filtered off. It can be further purified by dissolving it in hot water and precipitating again in the shape

of potassium salt by the addition of potassium chloride.

Subsequently the filtered sulphuric acid solution is run into water, the solution thus obtained is heated and from this hot solution the potassium salt of alpha$_1$ - alpha$_4$ anthraquinone disulphonic acid is precipitated in the shape of light yellow needles by the addition of potassium chloride.

Of course the separation of the two sulphonic acids can be carried out in another manner, for instance by a fractional crystallization of their salt.

Summary.

The new process for producing the alpha$_1$-alpha$_3$ and the alpha$_1$ - alpha$_4$ anthraquinone disulphonic acid, which process consists in first treating anthraquinone or anthraquinone alpha-monosulphonic acid with fuming sulphuric acid in the presence of mercury or mercury compounds until the disulphonation is completed,

and then separating the two resulting di-sulphonic acids from each other.

E. P. 25541 - 1903.

This patent on the production of anthrarufine states as follows:

On heating the anthraquinone - alpha - sulphonic acids, namely, the anthraquinone - alpha-mono-sulphonic acid, the $alpha_1$ - $alpha_3$ or the $alpha_1$ - $alpha_4$ anthraquinone disulphonic acids with oxides or hydroxides or alkaline earths and water the sulphonic groups are easily replaced by the hydroxy groups.

The anthraquinone -alpha-monosulphonic acid is thus converted into erythro-oxyanthraquinone, the $alpha_1$ - $alpha_3$ - anthraquinone disulphonic acid into anthrarufine and the $alpha_1$ - $alpha_4$ anthraquinone disulphonic acid into chrysazine.

To illustrate the process for anthrarufine the following example is used:

Heat 20 parts of sodium salt of $alpha_1$ - $alpha_3$ anthraquinone disulphonic acid 30 parts of slaked lime $Ca(OH)_2$ and 400 parts

of water for twelve hours to 180 - 190° C. and on decomposing the resulting melt with hydrochloric acid anthrarufine is obtained.

E. P. 25738 - A.D. 1903.

100 parts of commercial lime salt of 1:5 anthraquinone di-sulpho-acid are stirred up in 500 parts of hot water, and in this are slaked 100 parts of lime, and then 30 parts of salt peter and 100 parts of a 20 per cent solution calcium chloride are added, and the whole is kept under pressure in the digester at a temperature of 180 - 220 degrees Celsius until there is no longer any trace of oxy-sulpho-acid. After the contents of the digester have been discharged and precipitated with hydrochloric acid the yield is about 50 parts of pure anthrarufine.

The claim is:

The improved manufacture of ortho-oxy-anthraquinones, ortho-meta-oxyanthraquinones, ortho-anthraquinone-oxysulpho-acids, and ortho-meta-anthraquinone oxysulpho-acids, according to which salt of alkali metal or salt of alkaline earth metal of the corresponding ortho-sulpho-acids or ortho-meta-sulpho-acids are

heated with or without addition of salt of alkaline earth metal and with or without addition of oxidizing agents, in the presence of water and under pressure with an hydroxide or hydroxide of alkaline earth metal.

E. P. 1062 - 1905.

This patent for the production of anthrarufine has claim on the use of following materials:

100 parts of a paste containing 44% of the potassium salt of alpha$_1$ - alpha$_3$ anthraquinone disulphonic acid, 90 parts of a 27 per cent caustic soda lye, 50 parts of barium chloride and 600 parts of water. The mixture is heated for twelve hours under a pressure of about 140 pounds.

The anthrarufine is then extracted by dilute sodium hydroxide.

G. P. 164292.

The production of (1:5) and (1:8) disulphonic acid may be obtained from corresponding dichloro-derivatives by treating them with sodium sulphite solution.

G. P. 167169

This patent states that 1:5 disulphonic acid may be obtained from 5 nitroanthraquinone - 1 - sulphonic acid bythe use of sodium sulphite solution.

The German Patent on the production of anthrarufine 157123 is similar to the English Patent 13808 of 1903 which has been described.

G. P. 72685

This patent of making (1:5)and (1:8) dinitroanthraquinone is described as follows: 10 parts of anthraquinone, 200 parts of sulphuric acid and 10 parts of dry sodium nitrate are mixed and the mixture kept at about 70° for twelve hours. It is then poured into water and the mixture of 1:5 and 1:8 dinitro anthraquinone is separated out.

G. P. 145238.

This patent has claim on the use of pyridine on (1:5) dinitroanthraquinone in the substitution of (NO_2) group by hydroxyl (OH) group.

The pyridine is heated with mixture of dinitro anthraquinone in autoclave for four hours at 190°.

The anthrarufine obtained by first distilling off the pyridine and extracting it with sodium hydroxide.

G. P. 158891.

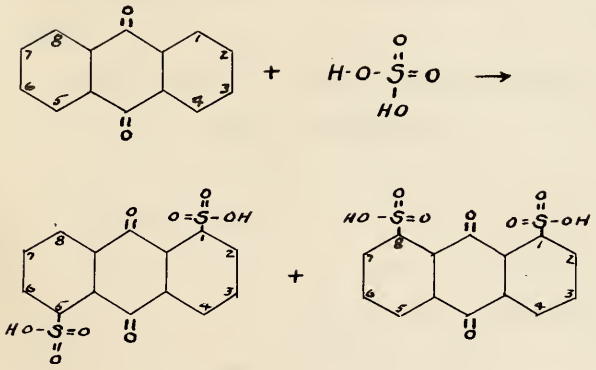
This patent has claim on the use of quick lime in the substitution of NO_2 group by OH.

The lime used is in proportion of 1:3. It is heated in an autoclave at 190° - 200°. The mass is then treated with hydrochloric acid and the anthrarufine extracted by use of sodium hydroxide.

Reactions and Considerations of

the Proposed Methods.

The general rules of introducing sulphonic acid group were discussed in the theoretical part of the thesis. The equation for the introduction of sulphonic acid group into anthraquinone is as follows:



The object in the use of mercuric salt is to obtain the 1:5 disulphonic acid of anthraquinone instead of (2 : 6) and (2 : 7) disulphonic acids of anthraquinone.

Separation of the Sulphonic Acid.

The separation of the sulphonic acids is based upon the solubility of 1 : 8 disulphonic anthraquinone in 60° Be sulphuric acid. Both acids of anthraquinone are soluble in water but the 1 : 5 disulphonic anthraquinone is insoluble in 60° Be sulphuric acid. Upon the above property the separation is carried out.

Substitution of SO_3H group by OH.

The proposed methods are:

1. By use; 27% NaOH solution

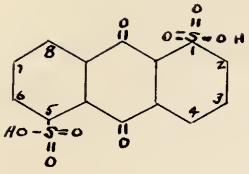
   Barium chloride

   Water.

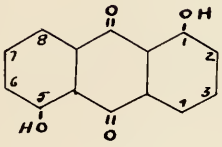
The heating to be conducted at 100° C and 150 pounds pressure for 15 hours.

2. By use; Milk of lime in proportion of 1 part of 1 : 5 anthraquinone disulphonate and 3 parts of lime at a temperature of 180° - 190°C in an autoclave with stirrer.

Reaction for replacement of SO_3H group by OH



$+ 2Ca(OH)_2 \rightarrow$



$+ 2CaSO_4$

Extraction of Anthrarufine.

1. By use of NaOH normal

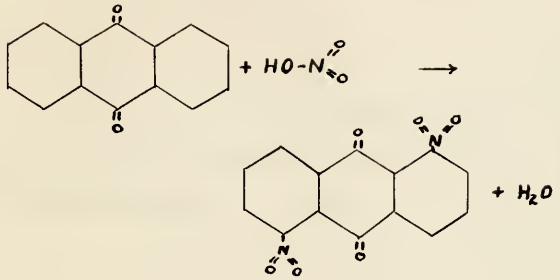
   By use of NaOH N/20

The anthrarufine is then precipitated by hydrochloric acid.

The Second Proposed Method.

By nitration of Anthraquinone

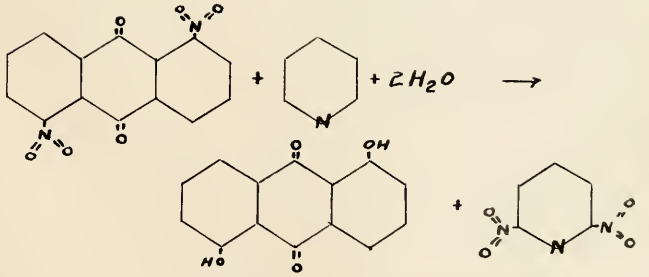
Reaction is as follows:



The anthrarufine is then made directly from the 1:5 dinitro anthraquinine by boiling it with pyridine in the proportion of 1 to 5.

The action of pyridine was discussed in the theoretical part of the thesis.

Reaction:



Pyridonium nitrate.

The pyridonium nitrate decomposes at the high temperature, such as used in the experiment, yielding pyridine which is then removed by distillation.

Extraction:

The extraction is done by the use of dilute sodium hydroxide and acidifying it with dilute hydrochloric acid.

Experimental.

First Run.

Raw Materials Used:

100 gms. Anthraquinone

2 gms. Mercuric Oxide

200 gms. Fuming Sulphuric Acid, containing 60% free SO_3

Procedure:

The anthraquinone was dissolved in the sulphuric acid and the mixture heated. The time and temperature ran as follows:

Time	Temperature
10:30	50° C.
10:45	74° C.
11:00	105° C.
11:15	120° C.
11:30	135° C.
11:45	161° C.
12:00	160° C.
12:15	172° C.
12:30	172° C.

At the end of the sulphonation as shown by a test, practically all of the free SO_3 has been absorbed. The above sulphonation was carried on with constant mechanical stirring. The contents of flask was then poured into 66° Be sulphuric acid.

Accordingly the crystals of 1:5 anthraquinone disulphonic acid should separate out. The mass has shown no appearance of any crystals under test with a microscope. The mass consisted of tar and was rejected. The reason for above error is high temperature and the high concentration of free sulphur trioxide in the sulphuric acid. The authors wish to remark that the sulphuric acid used in the above run was recommended in German Patent 157123. Furthermore, as seen from the table of temperatures in the course of sulphonation, at the temperature of 135°C. ther was a jump to 160° and with the burners removed it has still increased to 170° C.

Further work on the first run was dis continued and with the above points in mind the sulphonation of second run was started.

Second Run.

200 gms. Anthraquinone

4 gms. Mercuric oxide

400 gms. Fuming Sulphuric acid containing 50% Free SO_3.

Procedure:

The mixture was heated very carefully with constant stirring.

Time	Temperature
9:00	70°
9:15	83°
9:30	94°
9:45	125°
10:00	135°
10:15	158°
10:30	160°
10:45	155°
11:00	160°

The temperature was controlled so as not to exceed 160° C. as recommended by the English Patent 13808 of 1903 and the instructions written by John Cannell Cain. The reduction in temperature and the content of free SO_3 in the sulphuric acid has reduced the content of tar very considerably.

The 1:5 disulphonic anthraquinone was

poured into 60° Bé sulphuric acid, and the 1:5 disulphonate was separated from the 1:8 by filtration on asbestos. The 1:5 disulphonate was dissolved in hot water and precipitated as the potassium salt.

The 1:5 disulphonate was then dried and weighed. The yield was 82 gms.

Substitution of SO_3H by OH.

The 1:5 anthraquinone disulphonic acid was then mixed with 100 cc. of H_2O and made into a paste and put into the autoclave. 130 cc. of a 27% sodium hydroxide added and 95 gms. of barium chloride plus 1100 cc. of H_2O.

The mixture was heated to 100° C. under pressure of an average of 92 pounds for fifteen hours. The above pressure was the highest pressure obtainable in our laboratory. Under the above conditions the authors were unable to obtain any anthrarufine as it proved in the process of extraction.

Third Run.

Materials Used:

400 gms. Anthraquinone

2 gms. Mercuric oxide

800 gms. Fuming Sulphuric acid, containing 50% SO_3 free.

Procedure:

The mixture was heated up with more care to the desired point.

Time	Temperature
2:10	45° C
2:25	55°
2:40	68°
2:55	83°
3:10	99°
3:25	115°
3:40	128°
3:55	150°
4:10	155°
4:25	150°
4:40	153°

The time of sulphonation was increased, but the final temperature reached was the same. The color of solution was deepened to a dark red color rather than blackish red as found in other cases.

The mixture was then diluted with 60° Be sulphuric acid and the 1:5 anthraquinone disulphonic acid separated out. Dissolved in hot water and precipitated as potassium salt.

The 1:5 disulphonate was then dried and weighed. The yield was 214 gms.

Substitution of SO_3H by OH.

The use of milk of lime in the proportion of 3 parts of lime to 1 part of potassium disulphonic anthraquinone.

The mixture was placed in the autoclave and heated under pressure of 78 pounds and at temperature of 185° C average for twelve hours.

The mixture formed containing the anthrarufine was then boiled with sodium hydroxide.

One-half of the mixture boiled with normal sodium hydroxide while the other half with twentieth normal, and filtered separately

on the filter press (small)

Treatment with Hydrochloric Acid.of various strengths under different conditions in the Recovery of Anthrarufine.

The above two solutions were sub-divided into two parts each obtaining four portions.

First portion, strongly alkaline was treated with concentrated hydrochloric acid, but no anthrarufine separated out. It was then diluted on the second portion strongly alkaline but still anthrarufine did not separate out.

The third portion, just alkaline, was treated with concentrated hydrochloric acid and the anthrarufine started to precipitate out, but very slowly.

The fourth portion, just alkaline, was treated with very dilute hydrochloric acid and made just acid. The anthrarufine was pre-

cipitated without much difficulty. The yields are 17 gms. for the third portion, and 28 gms. for the fourth portion. Thus it showed an increase in yield of 66% in proportion.

Nitration Process.

Raw Materials:

200 gm. Anthraquinone

4000 gm. conc. Sulphuric Acid

200 gm. Dry Sodium Nitrate

The above materials were mixed and heated at a temperature of 60° to 80° C for twelve hours.

Time	Temperature
8:00 A.M.	30° C.
8:30	42°
9:00	47°
9:30	49°
10:00	53°
10:30	57°
11:00	57°
11:30	59°
12:00	57°
12:30 P.M.	59°
1:00	62°
1:30	67°
2:00	73°
2:30	76°
3:30	75°
4:30	74°
5:30	77°
6:30	76°
7:30	73°
8:30	77°

The mixture was then poured into water and the mixture of 1:5 and 1:8 dinitroanthraquinone

was filtered on the filter press (small laboratory size) and washed.

The mixture which contains 88% of the 1:5 compound and 12% of the 1:8 compound is used as such without purification in the preparation of anthrarufine.

The yield obtained was 145 gms. of dinitroanthraquinone.

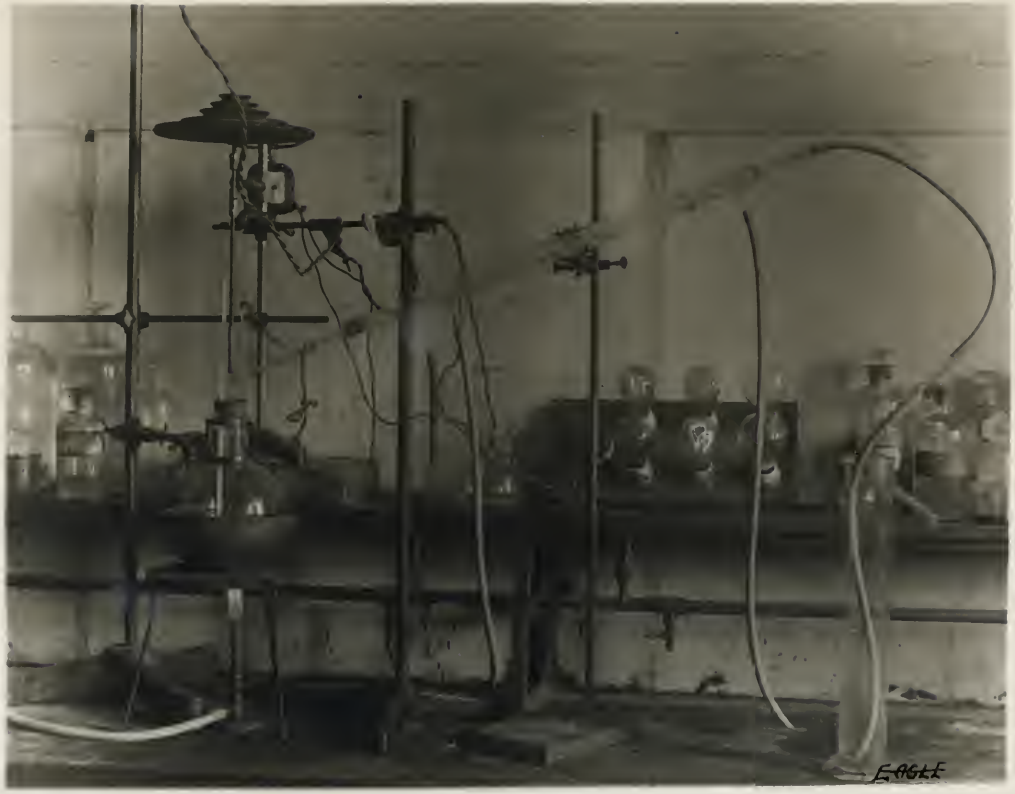
Replacement of NO_2 by OH.

The above material was then mixed with five times its quantity of pyridine in an autoclave for four hours at the average temperature of 180° - 200°.

Time	Temperature
12:00 P.M.	120° C.
12:20	138°
12:30	160°
12:50	185°
1:10	183°
1:30	180°
1:50	180°
2:10	176°
2:30	183°
2:50	179°
3:10	185°
3:30	187°
3:50	183°
4:10	189°
4:30	192°

The anthrarufine was then extracted by boiling with dilute sodium hydroxide and acidifying the solution with HCl.

The yield obtained is 23.2 gms. of anthrarufine.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Discussion on Experimental Work.

Each run has been discussed separately under the experimental work and in this paragraph it is the intention of the authors to draw up a discussion on the entire experimental work.

In sulphonation of anthraquinone the temperature and concentration of sulphur trioxide (free) must be regulated. This has been shown by the result of the first run. The temperature was too high and also the concentration (60% SO_3) of free sulphur trioxide. The mass formed after sulphonation was mostly tar. The authors failed to obtain the wanted product in the first run and with the above points in view have started on the second run.

In the second run the concentration of free sulphur trioxide was reduced to 50% and the temperature was controlled so as not to exceed 160° C. The time of sulphonation was two hours. The content of tar was reduced

considerably in the present run. The 1:5 and 1:8 disulphonic anthraquinone were separated on the bases of solubility in sulphuric acid 60^{o} Be. The yield of 1:5 disulphonate was 82 gms. and is 41% based on amount of anthraquinone used. The theoretical yield is 300 gms. Hence the products obtained is 27.3% yield of the theoretical. It was to the opinion of the authors that the yield could be increased by increasing the time of sulphonation.

The authors have used the method of sodium hydroxide treatment under pressure in the replacement of SO_3H by OH. They are failed to obtain the anthrarufine due to insufficient pressure available. In the opinion of the authors the product would have been obtained if a pressure of 140 - 150 pounds had been available.

The third sulphonation was carried on the same procedure as the second except its length of time was increased. The sulphonation

time was increased to two and one-half hours instead of two as in previous runs. The yield obtained was 214 grams which is 35.6% of theoretical. Thus the yield due to the increased time of sulphonation and a more regular temperature was increased 8.3%.

The substitution of SO_3H by OH was carried out by use of lime. The anthrarufine was obtained from the third and fourth portion of this run as described under the "Treatment with Hydrochloric Acid" in the third run.

The best conditions under which anthrarufine can be recovered is by the use of very dilute sodium hydroxide and very dilute hydrochloric acid. The product obtained under the best conditions as described above showed a practical yield of 37.3%.

The authors wish to say that the above product obtained under the most desirable conditions showed the color of anthrarufine to be ochre yellow.

The fourth run is the nitration run and was taken up by the authors to see whether a better yield could be obtained by this method. This process avoids the formation of any tar in the nitration process.

The yield of dinitroanthraquinone was 145 gms. which is 72.5% based on amount of anthraquinone used and is equivalent to a practical yield of 78.%. The theoretical amount of dinitroanthraquinone is 182 gms.

With the nitration process we have avoided the difficulty of handling the fuming sulphuric element. Nevertheless the compound pyridine showed some difficulty in its handling. The anthrarufine obtained from the nitration run is of red color instead of yellow which is the color of more or less pure anthrarufine.

The authors wish to remark that the above product contains a known impurity 1:8 dihydroxy anthraquinone (chrysazine)

which is a red product.

The anthrarufine weighed 23.2 grams which is a yield of only 20 per cent of theoretical.

Thus in conclusion we wish to say that the best yield was obtained in the third run.

The run in brief is:

The 50% free (SO_3) fuming sulphuric acid and in sulphonation temperature should not exceed 160° C.

In the substitution process use Ca(OH) lime and in heating acquire a temperature of 180° C. The recovery of anthrarufine is best by the use of dilute alkali and dilute acid.

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72685

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97688

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170118

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